Simultaneous DSC/TG analysis on the thermal behavior of PAN polymers prepared by aqueous free-radical polymerization

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A R T I C L E I N F O

A B S T R A C T

A series of polyacrylonitrile (PAN) polymers with different content of itaconic acid (IA) as comonomer were prepared by an efficient aqueous free-radical polymerization technique. The thermal behavior of the PAN polymers was investigated by simultaneous DSC/TG analysis. Effects of IA content, heating rate and atmosphere on the heat release and weight loss behaviors of the PAN polymers were studied for insight of the nature of the thermo-chemical reactions. A specific triple exothermic peak was observed in the DSC curves of P(AN-IA) copolymers in air atmosphere. Three individual exothermic peaks were obtained by peak fitting and assigned to the respective thermo-chemical reactions, namely, ionic cyclization reaction, free-radical cyclization reaction and oxidation reaction. The ionic cyclization reaction was significantly influenced by the IA content. The free-radical cyclization reaction was sensitive to heating rate and atmosphere. The cyclization reaction preceded the oxidation reaction and acted as a prerequisite for the oxidation reaction. The improvement of the thermal stability of PAN was mainly attributed to the oxidation reaction through dehydrogenation and formation of oxygen-bearing groups. Mechanisms of the thermo-chemical reactions were also proposed and discussed.

1. Introduction

Polyacrylonitrile (PAN) is the most important precursor polymer for preparation of high-performance carbon fibers [1]. Currently, almost 90% of commercial carbon fibers are produced from PAN [2]. Producing PAN-based carbon fibers involves the following steps: polymerization, spinning, thermal stabilization, and carbonization [3]. Among them, polymerization, as the first step, is of crucial importance, because the subsequent steps such as spinning and thermal stabilization, as well as the mechanical properties and production cost of final carbon fibers strongly depend on the PAN polymers [4].

Solution free-radical polymerization and aqueous free-radical polymerization are the two most commonly used techniques for production of PAN polymers [3]. The former is preferably adopted for preparation of high-performance carbon fibers due to a better controlling of the quality of precursor fibers. However, a long reaction time of about 20 h is involved in this technique to achieve a higher level of reaction conversion. Thus, the productivity is not satisfied for large volume production and cost control. In contrast, the aqueous free-radical polymerization is a highly efficient technique for production of PAN polymers. This technique is most commonly used for production of textile-grade acrylic fibers [3], because a very short reaction time of only about 1 h is needed to obtain a higher level of reaction conversion. Thus, this technique is preferably suitable for the large scale production of low cost carbon fibers [1].

Besides polymerization, the thermal stabilization is another crucial step for preparation of PAN-based carbon fibers [2,5]. It is generally carried out between 200 °C and 300 °C in an oxidizing atmosphere. During this process, PAN polymers undergo complicated thermo-chemical reactions and convert into infusible structure, so as to prevent the precursor fibers from fusing at elevated temperatures [6]. Optimization of the thermal stabilization process is necessary not only for improving the performance of the final carbon fibers, but also for reducing the production cost, because it is a extremely time-consuming and energy-consuming step [6]. The thermal stabilization process is highly dependent on the thermal behavior of PAN polymers [5]. The thermal stabilization conditions, including temperature, time and tension, must be optimized according to the thermal behavior of PAN polymers. The thermal

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behavior of PAN polymers have been investigated intensively in the last few decades [7–15]. However, because the thermal behavior depends closely on the nature and content of comonomers as well as the polymerization techniques of PAN polymers [5,14,16–20], there is still a lack of clarity about the thermo-chemical reactions hidden in the rear. At least three main issues remain to be studied. The first issue is what types of reactions really occur during the thermal stabilization. Generally, oxidation, dehydrogenation and cyclization are considered as the three major stabilization reactions [16,17,21,22]. But in fact, dehydrogenation is just a result of the oxidation reaction, since hydrogen is eliminated in the form of H_2O by reacting with oxygen [21]. In addition, cyclization can be further divided into ionic and free-radical two types, and both of them occur during stabilization. However, they are often confused or omitted. The second one is that the thermo-chemical reactions are carried out in what order and temperature range. A command of this knowledge is essential for optimizing the stabilization process [23]. The third one is what is the effect of each thermo-chemical reaction on the thermal stabilization process. The different types of reactions may generate different effects, such as varying degrees of heat release and weight loss, and formation of thermal stable structures or volatile fragments. In order to study these questions, it is necessary to separate the thermo-chemical reactions from each other. However, this is a difficult task because they are overlapped.

In the present study, we prepared a series of PAN polymers with different content of itaconic acid (IA) as comonomer by an efficient aqueous free-radical polymerization technique. The thermal behavior of the PAN polymers was investigated by simultaneous differential scanning calorimetry and thermogravimetry (DSC/TG) analysis. Effects of IA content, heating rate and atmosphere on the heat release and weight loss behaviors of the PAN polymers were studied. A triple exothermic peak was observed in the DSC curves of P(AN-IA) copolymers. Individual peaks were obtained by peak fitting and well assigned to the respective thermo-chemical reactions. By means of the simultaneous DSC/TG analysis technique, a deep investigation was made for insight of the nature of the thermo-chemical reactions, including defining the types of the thermo-chemical reactions, profiling their occurrence orders and corresponding temperature ranges, and clarifying their effects on the thermal stabilization process.

2. Experimental

2.1. Materials

Acrylonitrile (AN), purchased from Zhejiang Taizhou Zhonghai Pharmaceutical & Chemical Co., Ltd (China), was purified before use by vacuum distillation to remove the inhibitor. Itaconic acid (IA), with concentration of 99%, purchased from Aldrich Chemical Co., Inc. (USA), was used without further purification. Ammonium persulfate ($(NH_4)_2S_2O_8$) and ammonium sulfite ($(NH_4)_2SO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used as-received.

2.2. Polymerization

PAN polymers were prepared by an aqueous free-radical polymerization technique carried out in deionized water at 60 °C under nitrogen atmosphere for 60 min. $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_3$ were used as initiators. IA was used as comonomer. A series of PAN polymers with different content of IA were obtained after reaction followed by filtration, washing and drying at 60 °C under vacuum for 24 h.

2.3. Viscometry

The intrinsic viscosity ([η]) of the PAN polymers was measured at 30 °C in dimethylformamide (DMF) containing 0.1 g dL^{-1} of lithium bromide (LiBr). The viscosity average molecular weight (M_η) of the PAN polymers was calculated from [η] according to the following equation [24].

$$[\eta] = 3.35 \times 10^{-4} [M_\eta]^{0.75}$$

2.4. GPC

The molecular weight and its distribution of the PAN polymers were determined by gel permeation chromatography (GPC) (TOSOH HLC-8320GPC) with a refractive index detector. The samples were dissolved in 0.01 mol L^{-1} LiBr/DMF solution at 80 °C for 2 h at a concentration of 1 mg mL^{-1} and filtered using 0.45 μm PTFE syringe filter prior to analysis. The instrument was calibrated with a set of polystyrene (PS) standards which were purchased from TOSOH CORPORATION. The PS standards were dissolved at 80 °C for 2 h using 1.5 ml of 0.01 mol L^{-1} LiBr/DMF solution.

2.5. FTIR

FTIR spectra of the PAN polymers were recorded on a Thermo Nicolet Nexus 470 FTIR spectrometer using a thin film technique in 4000–400 cm^{-1} range. 32 scans were acquired at a resolution of 4 cm^{-1}. Thin films of PAN polymers were prepared by using a solution casting method as reported in the literature [25].

2.6. DSC/TG

DSC/TG analysis of the PAN polymers was carried out using a NETZSCH STA 449 thermal analyzer under air and nitrogen atmosphere at different heating rates of 5, 10, 15, and 20 °C min^{-1} from room temperature to 500 °C. The DSC parameters of the exotherms, including initiation temperature (T_i), peak temperature (T_{pk}) and heat evolved (ΔH) were obtained by the instrument software.

3. Results and discussion

3.1. Characterization of the PAN polymers by viscometry and GPC

The molecular weight and its distribution of the PAN polymers were determined by viscometry and GPC. The results are listed in Table 1. All the PAN polymers prepared by aqueous free-radical polymerization have a high molecular weight. The weight average molecular weight (Mw) is above one million for most of the PAN polymers. It is attributed to the low chain transfer constant of water, which is better for the chain propagation reaction during polymerization [1]. However, with the increase of IA content in feed, both the number average molecular weight (Mn) and Mw show a gradual decrease trend. The chain propagation reaction seems to be adversely affected by the IA comonomer, which may be due to the inhibition effect caused by its two bulky carboxylic groups. An appropriate reduction of the molecular weight is helpful to improve the solubility of the PAN polymers, which is necessary for obtaining high-quality precursor fibers.

3.2. Characterization of the PAN polymers by FTIR

Fig. 1 shows the FTIR spectra of the PAN polymers. The absorption at 2243 cm^{-1} is assigned to C≡N stretching vibration in

Table 1
Molecular weight of PAN polymers.

Code of samples	IA content in feed (wt%)	$[\eta]$ (dL g)$^{-1}$	M_η ($\times 10^4$)	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
PAN-homo[a]	0	8.42	129.3	/	/	/
P(AN-IA)-2	2	5.24	66.9	28.8	146.7	5.10
P(AN-IA)-3	3	5.19	66.0	24.0	105.0	4.37
P(AN-IA)-4	4	4.76	58.5	23.7	101.8	4.30
P(AN-IA)-5	5	4.60	55.9	21.2	97.8	4.61

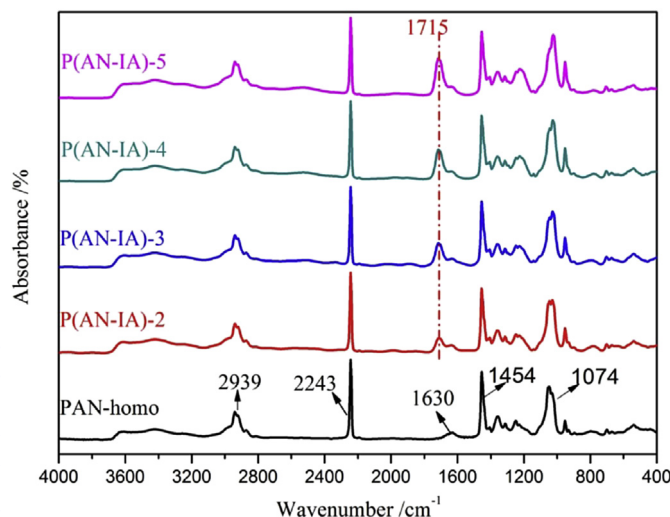[a] The PAN homopolymer was not characterized by GPC due to the poor solubility.

Fig. 1. FTIR spectra of PAN polymers.

Fig. 2. Plot of $A_{1715cm^{-1}}/A_{2243cm^{-1}}$ of P(AN-IA) copolymers versus IA/AN ratio in feed.

AN unit, the peak at about 1715 cm^{-1} is due to the C=O stretching vibration of −COOH in IA unit. The absorption bands of the stretching vibration and bending vibration of CH$_2$ are observed at 2939 and 1455 cm^{-1}, respectively. The assignments of other absorption bands can be found in Refs. [8,9,25]. With the increase of IA content in feed, the 1715 cm^{-1} band continues to increase. In the meantime, the 2243 cm^{-1} band gradually decreases in intensity. According to the Lambert-Beer's law, $A = \varepsilon bc$, where A is the absorbance, ε is the molar absorption coefficient, b is the thickness of film (cm), and c is the mole concentration (mol/cm). Since both $A_{1715cm^{-1}}$ and $A_{2243cm^{-1}}$ were determined by using the same film, namely with the same value of b ($b_{CO} = b_{CN}$), thus, the ratio of absorbance of these two bands is in proportion to the ratio of IA and AN in copolymer (x_{IA}/x_{AN}). A formula is shown as follows:

$$\frac{A_{1715cm^{-1}}}{A_{2243cm^{-1}}} = \frac{\varepsilon_{CO}b_{CO}c_{CO}}{\varepsilon_{CN}b_{CN}c_{CN}} = k\frac{x_{IA}}{x_{AN}}$$

where, $k = \varepsilon_{CO}/\varepsilon_{CN}$. This method can be used for quantitatively calculating the relative IA content. But of course it only can be used in the PAN samples with relatively lower IA contents [26,27]. At that condition, because of excess AN and just a small quantity of IA in the feed, all the IA can enters the chains. If the IA content in feed is two high, on the one hand IA will hinder the copolymerization reaction, on the other hand the unreacted IA or the generated IA oligomer may remain in the copolymer, which will affects the accuracy of this method.

The plot of $A_{1715cm^{-1}}/A_{2243cm^{-1}}$ of P(AN-IA) copolymers versus IA/AN ratio in feed is shown in Fig. 2. A good linear relationship can be found from Fig. 2. The IA content in P(AN-IA) copolymers increases in direct proportion to the increase of IA content in feed. Thus, it can be inferred that the IA unit is uniformly distributed along the chain.
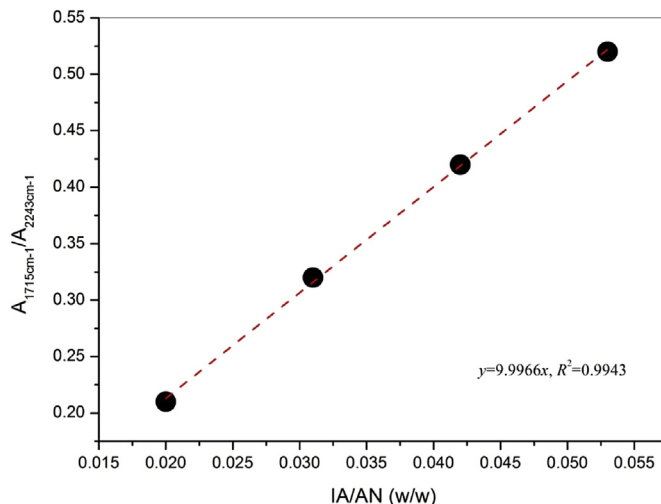
3.3. DSC/TG analysis at the same heating rate

Fig. 3 shows the DSC curves obtained at a heating rate of 10 °C/min in air atmosphere, and the corresponding parameters are listed in Table 2. As shown in Fig. 3, PAN homopolymer exhibits a sharp and narrow single exothermic peak, while the P(AN-IA) copolymers present a wide multiple feature. Several exothermic peaks emerge in the DSC curves of the P(AN-IA) copolymers, indicating the
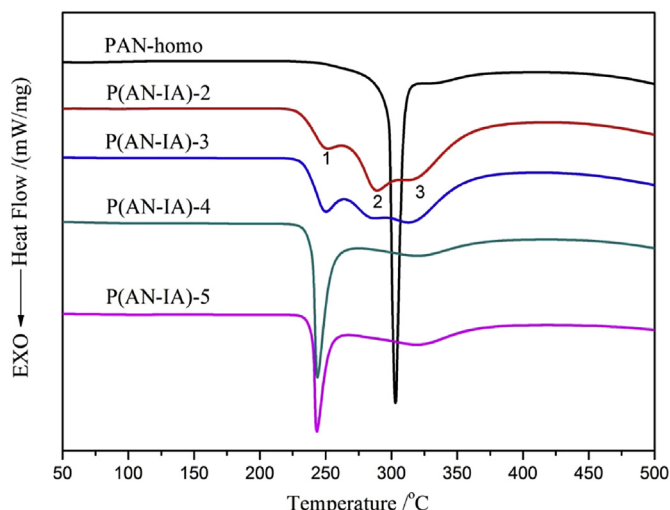

Fig. 3. DSC curves of PAN polymers at a heating rate of 10 °C/min in air.

Table 2
DSC parameters of PAN polymers at a heating rate of 10 °C/min in air.

PAN polymer	T_i (°C)	T_{pk1} (°C)	T_{pk2} (°C)	T_{pk3} (°C)	$-\Delta H$ (J/g)
PAN-homo	247.6	303.1	/	/	2589
P(AN-IA)-2	217.2	252.1	289.2	312.5	4639
P(AN-IA)-3	218.4	250.4	287.9	312.8	4160
P(AN-IA)-4	222.1	243.7	/	320.0	2926
P(AN-IA)-5	226.7	243.3	/	318.9	2503

T_i: initiation temperature of exothermic peak.
T_{pk1}, T_{pk2}, T_{pk3}: peak temperature of exothermic peak 1, 2, 3 as shown in Fig. 3.
ΔH: heat evolved.

presence of different kinds of thermo-chemical reactions. P(AN-IA)-2 and P(AN-IA)-3 show a distinct triple exothermic peak, which is quite different from the P(AN-IA) copolymers prepared by solution polymerization as reported in the literature [13,25,28]. Interestingly, the exothermic peak located at about 250 °C (Peak 1) grows significantly with the increase of IA content in feed. Thus, this peak may be assigned to the cyclization reaction which is initiated by the IA comonomer. This kind of cyclization reaction is generally considered to be followed an ionic mechanism at a lower temperature [13,25,28].

The incorporated IA comonomer plays an important role in lowering the initiation temperature (T_i) of the exothermic peak. The T_i of PAN homopolymer is about 248 °C, while that of the P(AN-IA) copolymers decreases to about 220 °C. Among which, P(AN-IA)-2 presents a lowest T_i at about 217 °C. Compared to the PAN homopolymer, the T_i of P(AN-IA)-2 has decreased by more than 30 °C. It provides a wider operation temperature range for the thermal stabilization process. When the thermal stabilization is carried out at lower temperature, it helps to avoid excessive heat eruption and obtain a homogeneous stabilized structure. However, when the IA content in feed increases beyond 2%, Ti has conversely increased to some extent. It means too much IA will spoil the effect. In addition, the heat evolved (ΔH) has decreased significantly with increasing IA content. As the IA content increases from 2% to 5%, ΔH decreases from 4639 J/g to 2503 J/g. It means that incorporation of excess IA comonomer reduces the extent of the thermo-chemical reactions. The similar phenomena have been observed by other researchers [17,28], which may be attributed to the interruption in the sequence distribution of AN units in the polymer chain by the IA units.

Fig. 4 shows the TG curves obtained synchronously with the DSC curves as shown in Fig. 3. The TG curves corresponding to weight loss can be roughly divided into three stages. As for PAN homopolymer, the first stage is up to 300 °C. In this stage, the weight loss is quite small. The second stage is from 300 °C to 305 °C. In this stage, PAN homopolymer takes place a sudden and steep weight loss. The weight loss is more than 20%. Because this stage is just corresponding to the DSC exothermic peak (T_{pk} = 303 °C), the weight loss must be related to the violent heat release caused by the thermo-chemical reactions. In the third stage above 305 °C, the weight loss takes place at a relatively steady pace.

P(AN-IA) copolymers show significant differences from PAN homopolymer in the weight loss, especially at the second stage. P(AN-IA)-2 and P(AN-IA)-3 start weight loss at about 270 °C. At this stage, the weight loss is obvious, but much lower than that of PAN homopolymer. It may be attributed to the absence of violent heat release. P(AN-IA)-4 and P(AN-IA)-5 firstly show a stage of sudden weight loss at about 240 °C as the PAN homopolymer, and then followed by a comparatively slower weight loss as P(AN-IA)-2 and P(AN-IA)-3. Both P(AN-IA)-4 and P(AN-IA)-5 have high IA comonomer content, and more carboxyl groups are located in the side chain. The sudden weight loss at about 240 °C may be due to the dehydration reaction and decarboxylation reaction of the carboxyl groups, which results in evolution of H_2O and CO_2 [6,13,29].

3.4. DSC analysis at different heating rates

The above DSC/TG results have confirmed the content of the incorporated IA comonomer should not be too high. P(AN-IA)-2 exhibits the preferable thermal behavior, and is therefore selected for making further research. In order to clarify the characteristics of the triple exothermic peak, a series of DSC curves of P(AN-IA)-2 were obtained by scanning at different heating rates. Fig. 5 shows the DSC curves of P(AN-IA)-2 at heating rates of 5, 10, 15, and 20 °C/min in air atmosphere, and the corresponding parameters are listed in Table 3. As shown in Fig. 5, with the heating rate increasing, the exothermic peak wholly shifts to a higher temperature. As listed in Table 3, both the initial temperature (T_i) and peak temperature (T_{pk}) increase significantly with the increase of heating rate. This phenomenon has been also reported in the literature and generally attributed to the delay of heat transfer [28]. The heat evolved (ΔH) firstly decreases with the increase of heating rate from 5 to 15 °C/min, and then increased to some extent with further increasing the heating rate to 20 °C/min. It is consistent with the results of previous studies [28].
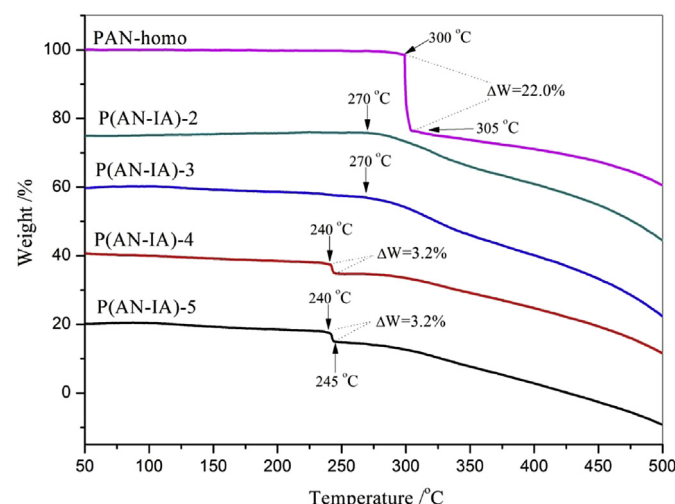

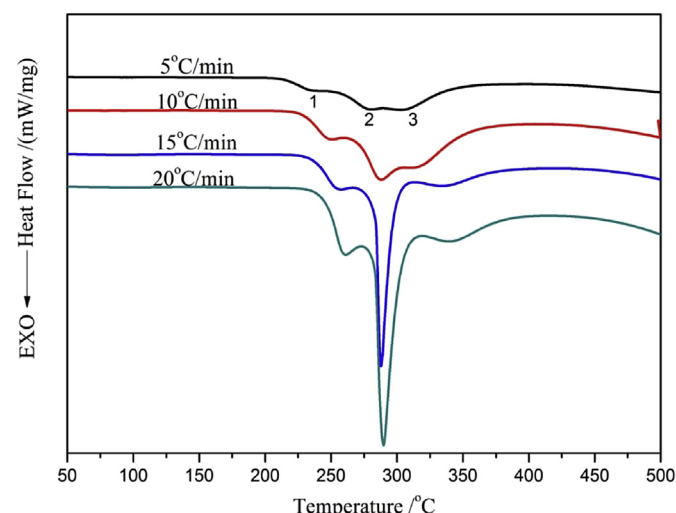**Fig. 4.** TG curves of PAN polymers at a heating rate of 10 °C/min in air.

Fig. 5. DSC curves of P(AN-IA)-2 at different heating rates in air.

Table 3
DSC parameters of P(AN-IA)-2 at different heating rates in air.

Heating rate (°C/min)	T_i (°C)	T_{pk1} (°C)	T_{pk2} (°C)	T_{pk3} (°C)	$-\Delta H$ (J/g)
5	202.7	239.0	280.5	303.0	4588
10	213.0	250.6	287.8	311.1	4409
15	227.0	255.7	287.9	333.9	3022
20	228.7	260.9	289.8	339.4	3630

T_i: initiation temperature of exothermic peak.
T_{pk1}, T_{pk2}, T_{pk3}: peak temperature of exothermic peak 1, 2, 3 as shown in Fig. 5.
ΔH: heat evolved.

With the increase of heating rate, the first exothermic peak (T_{pk1}) and the second exothermic peak (T_{pk2}) are gradually enhanced. In particular, T_{pk2} is more prominent than T_{pk1}. At the heating rate of 5 °C/min, T_{pk2} is not outstanding, but when the heating rate is increased to 10 °C/min, it begins to become significant. At the heating rate of 15 °C/min, T_{pk2} becomes more and more strong, over the other two exothermic peaks. The cyclization reaction, as an intramolecular polymerization reaction, is commonly considered to be mainly sensitive to temperature. From the results of Fig. 3, T_{pk1} is assigned to the ionic cyclization reaction. Thus, T_{pk2} is likely to be attributed to the free-radical cyclization reaction. Generally, the former induced by the IA comonomer can be carried out at a lower temperature with a slow pace, while the latter can only be taken place at a higher temperature because of the higher reaction activation energy. The primary free radicals which are necessary for inducing the free-radical cyclization reaction, can be formed only in the high temperature condition. However, once the free radical cyclization reaction is initiated, it will propagates rapidly, resulting in a large amount of heat being evolved

simultaneously. A higher heating rate makes the cyclization reaction, especially the free-radical cyclization reaction, more violent, and correspondingly the exothermic peaks become more sharp and recognizable.

T_{pk3} may be attributed to the oxidation reaction, which is controlled by the diffusion of oxygen. Therefore, it is not so sensitive to the increase of heating rate as the other two exothermic peaks. Oxidation reaction generally follows the cyclization reaction. Cyclization is considered as a prerequisite for the oxidation reaction [30]. Oxidation reaction prefers to take place with cyclized PAN rather than uncyclized PAN chains [5].

3.5. DSC/TG analysis under different atmospheres

In order to further confirm the assignment of the three exothermic peaks of P(AN-IA)-2, DSC/TG analysis of PAN homopolymer and P(AN-IA)-2 in different atmospheres has been carried out. Fig. 6(a)–(d) show the DSC/TG curves of PAN homopolymer and P(AN-IA)-2 in nitrogen and air atmospheres, respectively. PAN homopolymer exhibits a single sharp and narrow exothermic peak in nitrogen. Because there are no comonomers and oxygen, this peak can be attributed to the free-radical cyclization reaction only. The exothermic peak starts at about 231 °C. It is earlier than the exothermic peak in air which starts at about 248 °C (as shown in Fig. 6(b)). Thus, it can be inferred that the free-radical cyclization reaction in air may be inhibited to some extent by oxygen which is known as an inhibitor to various free-radical reactions [31]. As can be seen from Fig. 6(a), the most intense heat release appears at about 274 °C (T_{pk}), almost simultaneously, a severe weight loss begins to erupt. The cyclization reaction is generally considered to
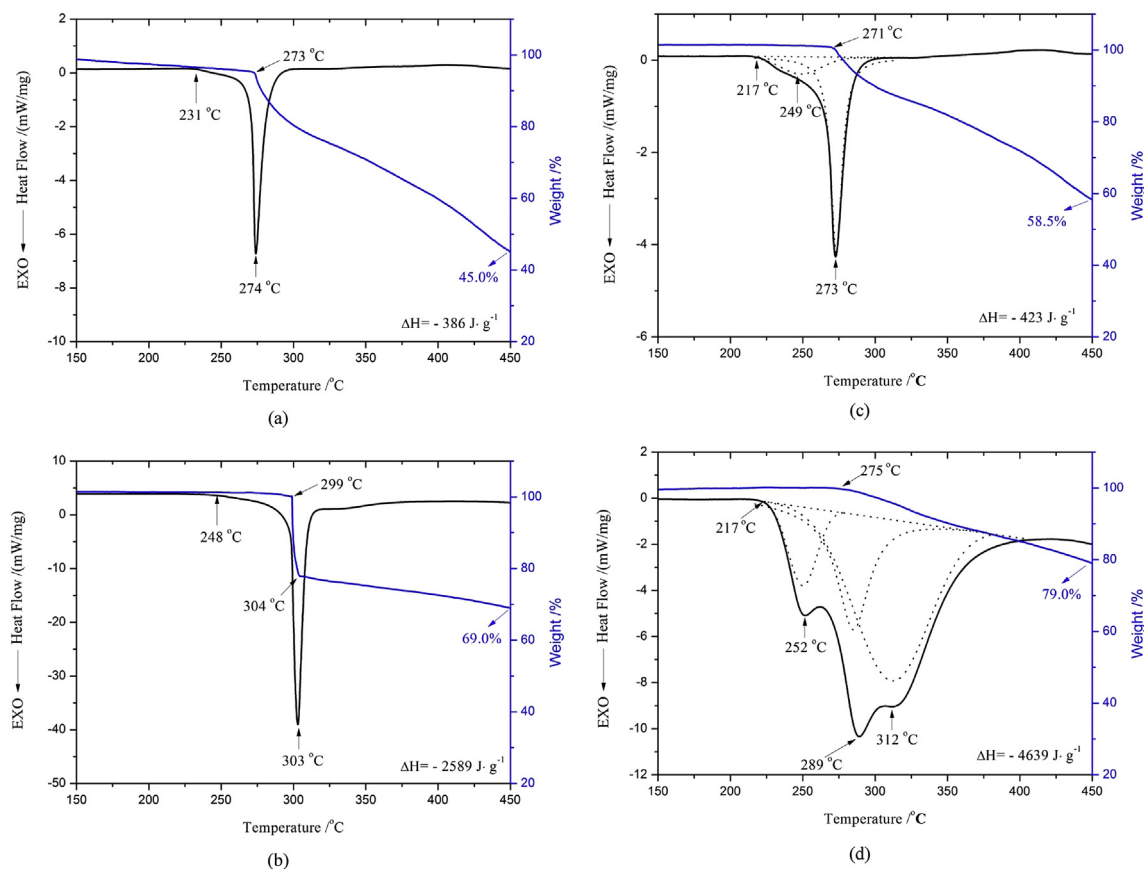

Fig. 6. DSC/TG curves of PAN-homo in nitrogen (a) and air (b), and P(AN-IA)-2 in nitrogen (c) and air (d) at heating rate of 10 °C/min.

be not a cause of weight loss. However, here we can concluded the free-radical cyclization reaction may be a predominate cause of weight loss. The free radicals seem to not only play roles in initiating the cyclization reactions, but also act as kindling to ignite other degradation reactions.
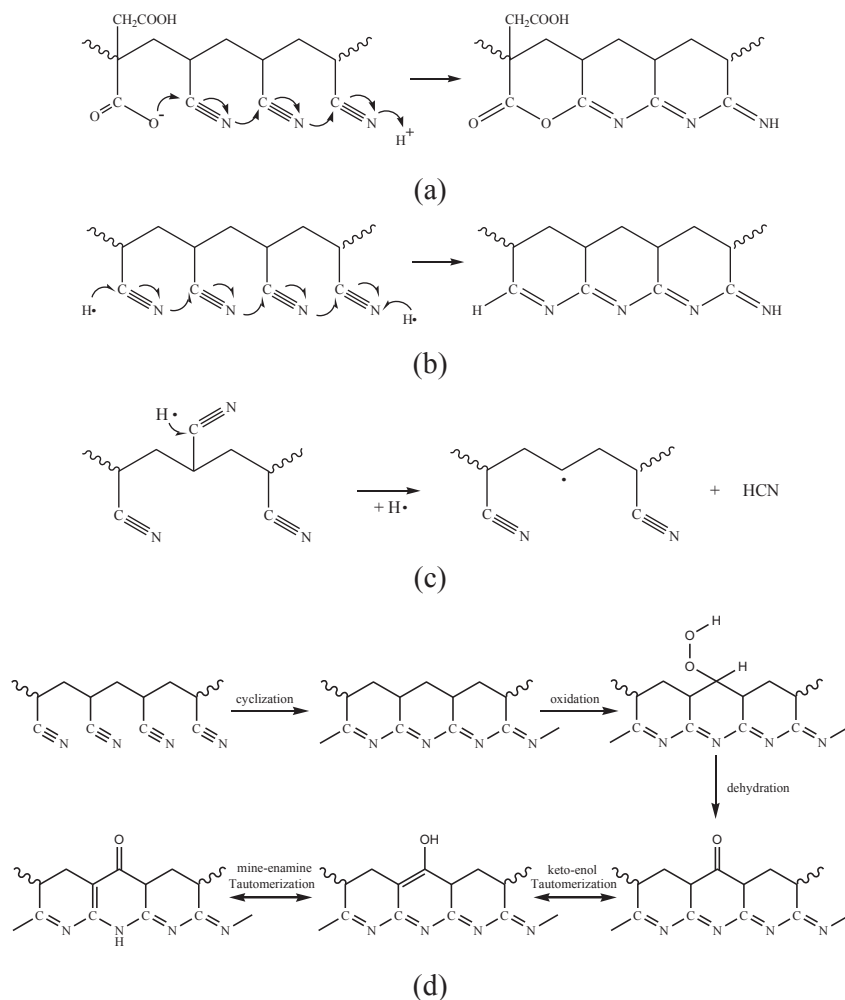
As shown in Fig. 6(b), PAN homopolymer also exhibits a singe sharp and narrow exothermic peak in air. In the air, oxygen is involved in the oxidation reaction. It indicates the free-radical cyclization reactions has overlapped with the oxidation reaction, which leads to more intense heat release and a cliff-like weight loss. However, the final weight residual at 450 °C in air is much more higher than that in nitrogen. It may be mainly contributed to the oxidation reaction which is a major factor leading to weight gain through the generation of oxygen-bearing groups. The introduction of oxygen element through the oxygen uptake reactions has offset partial weight loss [28,32].

As shown in Fig. 6(c), P(AN-IA)-2 has a strong exothermic peak at about 273 °C (T_{pk2}) and a weak shoulder at about 249 °C (T_{pk1}) in nitrogen. The former can be assigned to the free-radical cyclization reaction since it looks like the exothermic peak of PAN homopolymer in nitrogen. The shoulder may be due to the ionic cyclization reaction which is initiated by the IA comonomer. It starts at an earlier temperature ($T_i = 217$ °C) because of lower activation energy. The weight loss begins at 273 °C, just corresponding to the

T_{pk2}. It can be concluded that the free-radical cyclization reaction can lead to severe weight loss, while the ionic cyclization reaction does not cause weight loss.

As can be seen in Fig. 6(d), P(AN-IA)-2 shows a triple exothermic peak in air. The newly appeared peak at about 312.5 °C is certainly caused by the oxidation reaction, since this peak is not found in the Fig. 6(c). In the air atmosphere, the total heat release ($\Delta H = -4639$ J/g) is much larger than that of the nitrogen ($\Delta H = -423$ J/g). It indicates the oxidation reaction is mainly responsible for the heat release. Even both in the air, the total heat release of P(AN-IA)-2 is much larger than that of the PAN homopolymer. Oxidation reaction is more likely to be carried out in the former. It is probably due to the cyclization reaction of former is more effective than that of latter. In nitrogen, the total heat release of P(AN-IA)-2 is much larger than that of the PAN homopolymer.

The first two exothermic peaks at 252 and 289.2 °C belong to the ionic cyclization reaction and free-radical cyclization reaction, respectively. The first exothermic peak starts at 217 °C as the same as that in nitrogen. It implies that the initiation of the ionic cyclization reaction is not affected by oxygen. However, both the two exothermic peaks have been enhanced in air atmosphere as compared with that in nitrogen atmosphere (Fig. 6(c)). It seems that both the ionic cyclization reaction and free-radical cyclization reaction are promoted by the oxidation reaction, which is probably

(a)

(b)

(c)

(d)

Scheme 1. Mechanisms of the thermo-chemical reactions. (a) COOH-induced ionic cyclization reaction. (b) Free-radical cyclization reaction initiated by •H. (c) Free-radical decomposition reaction initiated by •H. (d) Oxidation reaction and successive tautomeric changes.

due to the effect of heat release caused by the oxidation reaction.

The weight loss also starts at the point corresponding to the second peak, indicating the weight loss is mainly caused by the free-radical cyclization reaction. As the same with PAN homopolymer, the final weight residual at 450 °C of P(AN-IA)-2 in air is much more higher than that in nitrogen. It confirms that oxidation reaction is conducive to reducing weight loss.

3.6. Mechanisms of the thermo-chemical reactions

It is widely accepted that in P(AN-IA) copolymer the cyclization reaction of nitrile groups can be initiated at a lower temperature through an ionic mechanism (Scheme 1(a)) [2]. The hydroxyl oxygen of −COOH in IA unit makes a nucleophilic attack on the carbon atom of an adjacent nitrile group and induce it to cyclize with the other one, which leads to formation of a ladder polymer structure through oligomerization of −C≡N groups to −C=N− groups [2].

In PAN homopolymer, the cyclization reaction of nitrile groups only can be initiated at a higher temperature through a free radical mechanism [13]. The initial free radicals are possibly generated by the homolytic thermal cleavage of weak bonds, such as terminal groups and side groups. A specific free-radical cyclization reaction initiated by the common free radical ·H is shown in Scheme 1(b).

Previous DSC and TG results have indicated that free-radical cyclization reaction is accompanied with thermal decomposition reaction, which leads to severe weight loss. The initial free radicals can initiate not only the cyclization reaction, but also the decomposition reaction. The latter involves the release of gaseous and volatile by-products. Such as hydrogen cyanide (HCN), which is the main toxic by-product during the thermal stabilization process [33]. A free-radical reaction pathway is proposed as shown in Scheme 1(c). When a initial free radical ·H attacks the carbon atom of an isolated nitrile group, HCN is formed.

The oxidation reaction mechanism is shown in Scheme 1(d), which is proposed by Watt and Johnson [30]. They believe that formation of ladder polymer is a prerequisite to oxidation, which is consistent with the above results as shown in Fig. 6(d). When the ladder polymer reacts with oxygen in air, a hydroperoxide is formed. After dehydration, the hydroperoxide changes to a pyridone. The pyridone may be converted into hydroxyl pyridine and pyridone by keto-enol tautomerism and mine-enamine tautomerism, respectively.

The oxidation reaction plays two important roles during the thermal stabilization. One is dehydrogenation. Hydrogen, as an unnecessary heteroatom for final carbon fibers, is eliminated in the form of H_2O through reacting with oxygen, giving conjugated C=C structures on the chain backbone. The other is formation of oxygen-bearing groups, such as >C=O and −OH, which leads to a certain extent of weight gain [28,32]. These oxygen-bearing groups promote further intermolecular crosslinking of the ladder polymers and provide greater thermal stability to sustain the high temperature during carbonization treatment [4].

4. Conclusions

The specific triple DSC exothermic peak of the P(AN-IA) copolymers in air atmosphere have been resolved into three individual peaks and assigned to the respective thermo-chemical reactions. The first exothermic peak was assigned to the ionic cyclization reaction initiated by the IA comonomer at a lower temperature. It was significantly influenced by the IA content. The intermediate exothermic peak was attributed to the free-radical cyclization reaction. It was sensitive to heating rate and atmosphere. The free-radical cyclization reaction was accompanied with thermal decomposition reaction, which led to severe weight loss.

The final exothermic peak was caused by the oxidation reaction, which was mainly responsible for the heat release and weight gain. The cyclization reaction preceded the oxidation reaction and acted as a prerequisite for the oxidation reaction. The improvement of the thermal stability of PAN was mainly attributed to the oxidation reaction through dehydrogenation and formation of oxygen-bearing groups.

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